Landau Expansion for the Critical Point of a Polydisperse System

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The effect of polydispersity on the phase diagram of a simple binary mixture is to split the binodal curve into cloud and shadow curves that cross at the critical point (which, in general, is not at the maximum of either curve). Recent theories of polydispersity have shown, in favorable cases, how to project the (infinite-dimensional) free energy of the polydisperse system into a low dimensional space of `moment densities'. We address here the issue of how to construct a Landau expansion from the projected free energy. For the simplest case where the excess free energy depends on one moment density (this includes Flory Huggins theory for length-polydisperse chains) we show that the minimal expansion remains quartic in the moment density but nonetheless has seven independent coefficients, not two. When this expansion is handled correctly all the peculiar qualitative features of the polydisperse phase diagram are recovered, as are the slopes of the cloud and shadow curves, and the curvature of the cloud. However, to correctly predict the curvature of the shadow, certain fifth order terms must be retained. We also consider the phase diagram on the temperature-pressure plane, where the coexistence line broadens into a region. In general, the critical point lies between the point of maximum temperature and the point of maximum pressure on the perimeter of this region. This behavior is again captured by the Landau expansion.